Real-time Synchrotron X-ray Powder Diffraction Study of the Structure and Dehydration of Todorokite

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Introduction: Todorokite is a major phase in ocean Mn nodules and also commonly occurs in the oxidized zone of terrestrial Mn-rich deposits. Because of todorokite's large zeolite-like tunnels, there is considerable interest in investigating synthetic analogues for possible use as catalysts and molecular sieves. Unfortunately, all known natural and synthetic todorokite specimens are fine-grained and/or poorly crystalline and not suitable for single-crystal studies; consequently, many aspects of the todorokite crystal structure and behavior are poorly understood. In the current study, temperature-resolved, in situ powder X-ray diffraction data were collected at the National Synchrotron Light Source using imaging plates to investigate the structures and dehydration properties of todorokite from South Africa. Samples were heated to 400 ºC in glass capillaries in air and under vacuum, and in some cases effluents were monitored by mass spectrometry. The imaging-plate data provide nearly continuous diffraction records versus temperature, making it possible to investigate structural changes, including phase transitions, with unprecedented detail. The todorokite structure changes only slightly up to about 275 ºC, and then collapses, coincident with release of water. By about 300 ºC, hausmannite starts to form and remains to 400 ºC. Rietveld refinements of the RT pattern and a data set collected at near liquid nitrogen temperature provide a much more precise structure than previous studies and considerably more detail about the tunnel water and cation positions. Refinements of the high temperature data show a gradual flexing of the structure prior to collapse.

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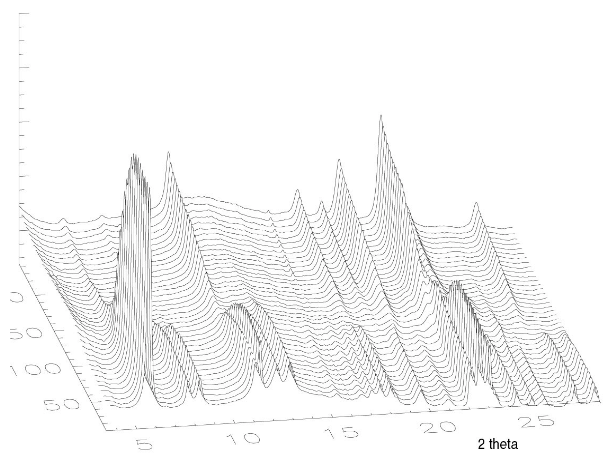

Figure 1. Time-resolved XRD patterns obtained between 25 and 400°C.